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⑯ Corrosion-resistant aluminium core alloy.

⑰ An aluminium alloy contains vanadium as an alloying element. The vanadium is preferably at a concentration in the range from 0.02% to 0.4% by weight and imparts corrosion-resistance to the alloy, particularly when it is used as a core alloy in a vacuum brazing sheet. Further corrosion resistance is also achieved by processing the alloy or brazing sheet in such a manner that the final processing step is a cold working effected so as to reduce the sheet by 10% to 20%.

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CORROSION RESISTANT ALUMINUM CORE ALLOY

BACKGROUND OF THE INVENTION

1. Field of the Invention

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This invention relates to aluminum alloys, and particularly to aluminum alloys used in corrosive environments.

10 2. Description of the Relevant Art

15 Aluminum has long been known for its resistance to corrosion, a property which renders it a favorable material of construction for a wide variety of purposes. In particular, it has gained wide acceptance in the manufacture of heat exchangers such as, for example, automotive radiators and evaporators for air conditioning units. Depending on the type of exchanger, the parts may be joined together by welding or brazing.

20 Despite aluminum's inherent corrosion resistance, corrosion still occurs. This is particularly true in materials joined by brazing, since the brazing operation causes intergranular penetration of the core material by certain species in the brazing alloy, notably silicon. When the brazed product is subjected to a corrosive environment, the intergranular regions in the core, where silicon is present in high concentrations, are particularly susceptible to corrosion. In automotive radiators, for example, where the brazing alloy is present only on the exterior surface of the tubes, the salts and moisture from the road are sufficiently corrosive to cause attack from the outside, resulting ultimately in pinhole formation.

25 This problem has been addressed in the literature in a variety of ways. An early example is Miller, U.S. Patent No. 2,821,014 (January 28, 1958), where it is disclosed that intergranular corrosion problems in flux and dip brazing are alleviated by adding an inter layer between the structural member portion and the brazing layer. The interlayer is aluminum or an aluminum-base alloy, particularly certain magnesium-containing alloys, having a melting point greater than that of the structural alloy. The solution offered by Singleton et al., U.S. Patent No. 3,788,824 (January 29, 1974) and its divisional, No. 3,881,879 (May 6, 30 1975), is directed to vacuum brazing, and involves the addition of iron to either the core alloy or the cladding alloy as an alloying element, resulting in improvements in both corrosion resistance and sag resistance.

35 Anthony et al., U.S. Patent No. 4,039,298 (August 2, 1977) address both flux and vacuum brazing, and disclose a composite of complex and highly specified composition as being particularly beneficial in terms of corrosion properties. The disclosed core alloy contains specified amounts of manganese, copper, chromium, silicon and iron as alloying elements with both a solid solution and an alpha-phase, whereas the alloying elements in the cladding are bismuth and silicon. An additional disclosure by the same patentees appears in U.S. Patent No. 4,093,782 (June 6, 1978) and its continuation-in-part, No. 4,167,410 (September 11, 1979), in which the core alloy contains a specified combination of chromium and manganese, with 40 resultant improvements in both corrosion resistance and sag resistance.

45 A still further disclosure by the same patentees appears in U.S. Patent No. 4,209,059 (June 24, 1980), where a conventional core alloy is clad with a brazing alloy on one side and a "sacrificial cladding layer" on the other, the result being a lessening of crevice corrosion between the aluminum header plate and the plastic tank in an automobile radiator. A "sacrificial anode" effect is disclosed in Tanabe et al., U.S. Patent No. 4,317,484 (March 2, 1982), and Terai et al., U.S. Patent No. 4,203,490 (May 20, 1980), for tube-and-fin heat exchangers by incorporating tin and zinc into the fin core material and manganese into the tube material. A similar differentiation between fins and tubes is disclosed in Kanada et al., U.S. Patent No. 4,410,036 (October 18, 1983), whereby the fins are provided with a lower electrochemical potential.

50 Setzer et al., U.S. Patent No. 3,994,695 (November 30, 1976), disclose a core alloy which contains a chromium-manganese-zirconium combination, the sole claimed benefit however being an improvement in sag resistance. Sag resistance is also addressed by Toma et al. in U.S. Patent No. 4,511,632 (April 16, 1985), where manganese, silicon and zinc are included in the cladding layer. A combination of copper and titanium as primary alloying elements in the core alloy is disclosed in Kaifu et al., U.S. Patent No. 4,339,510 (July 13, 1982), as providing a benefit in intergranular corrosion resistance.

A different approach is disclosed by Nakamura, U.S. Patent No. 4,172,548 (October 30, 1979), in which corrosion following fluxless brazing processes in general (including both vacuum brazing and brazing in an inert atmosphere) is controlled by controlling the grain size of the brazing sheet to at least 60 microns in diameter, achieved by a controlled cold work followed by a full anneal.

5 Thus, with the exception of Nakamura, existing solutions generally involve the introduction of specific elements in the alloy compositions. Processing modifications have also been used to similar effect, notably that disclosed in copending, commonly owned application Serial No. 634,529, filed July 26, 1984. In general, however, such features as specific combinations, degrees and sequences of strain hardening and annealing are generally used for controlling the ductility and tensile properties of the final product. Setzer et al., referenced above, demonstrates several of these combinations, ranging from those ending with a fully hardened product (maximum cold work) to those ending with a fully strainfree (annealed) product. The use of a partial anneal as the final step to leave the desired amount of cold work remaining in the product is disclosed by Singleton, U.S. Patent No. 3,963,454 (June 15, 1976) at column 4, lines 34-58.

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SUMMARY OF THE INVENTION

It has now been discovered that the introduction of vanadium as an alloying element enhances the corrosion resistance of aluminium and aluminum alloys. In particular, brazing sheets containing such alloys 20 as core alloys are unusually resistant to corrosion even after vacuum brazing. It has further been discovered that corrosion resistance is improved even more by the inclusion of a final cold work step to a reduction ranging from about 10% to about 20%.

25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The amount of vanadium in the alloy is not critical to the invention and may vary considerably. In most applications, however, amounts ranging from about 0.02% to about 0.4% by weight, preferably from about 0.05% to about 0.3%, will provide the best results.

30 The remainder of the alloy may vary widely in composition, although those alloys containing silicon, manganese, magnesium or combinations of these as the primary alloying elements, i.e., the components present in the highest concentrations other than the aluminum itself, are preferred. The concentrations of these elements may vary widely but typically range from about 0.2% to about 2.0% by weight. In preferred embodiments, the core alloy is a non-heat-treatable alloy, most preferably of the 1XXX, 3XXX or 5XXX 35 series of Aluminum Association designated alloys. Examples are the 1100, 3003, 3005, 3105, and 5005 alloys.

In embodiments where the alloy is clad for brazing, the cladding alloy (also referred to herein as a "brazing alloy") may be any aluminum alloy capable of flow under brazing conditions to form fillets at the 40 contact points sufficient to produce a sturdy bond. Such alloys will generally contain silicon as the primary alloying element, preferably at a concentration ranging from about 5% to about 15% by weight. Examples of such alloys are those of the 4XXX series, e.g., 4004, 4043, 4045, 4047, 4104 and 4343.

45 Brazing sheets of particular interest are those having a hardness ranging from fully annealed to about three-quarters hard. For example, air-conditioning evaporators require fully annealed metal, whereas for radiators one-quarter to three-quarters hard is preferred. As known to those skilled in the art, full hard is recognized in the industry as being equivalent to the hardness of a product which has been cold worked to a 75% reduction. In more preferred embodiments of the invention, the final brazing sheet is approximately one-half hard, i.e., ASTM temper designation H14.

50 As mentioned above, preferred embodiments within the scope of the invention are those where the processing includes rolling the alloy or composite to form a sheet product, annealing the sheet product to a strain-free state, and finally cold working the annealed product to a reduction of about 10% to about 20%. The rolling step may include a number of substeps, including a hot working to bond the cladding to the core, a scalping or etching to remove the oxide formed on the surface during the hot working, and a cold working to bring the gauge down to a value somewhat higher than the desired ultimate value, so that the full anneal and final cold working will produce both the hardness and gauge sought.

55 The cold working and annealing steps may be done according to conventional techniques well known to those skilled in the art. The annealing is generally done at a temperature of from about 500°F to about 850°F (260°C to 427°C), for a period of time ranging from about 0.5 hours to about 5 hours, preferably from about 600°F to about 700°F (316°C to 371°C) for about 1 to 3 hours.

For embodiments involving composite sheets, the cladding layer generally forms from about 0.1 percent to about 20 percent, preferably from about 1.0 percent to about 15 percent, of the thickness of the entire composite, and is present on one or both sides of the core, depending on the intended use of the brazing sheet. The bonding of the cladding to the core is typically achieved by conventional hot rolling techniques at temperatures ranging from about 450°F to about 1,000°F (230°C to 540°C). The cladding may be preceded by homogenization of the core typically at a temperature within the approximate range of from 800°F to 1150°F (427°C to 621°C), although in some alloys and procedures corrosion resistance will be improved by omitting the homogenization step.

5 Cold working is generally done by rolling, stretching or forming at ambient temperature. In general, the initial cold work step (prior to the full anneal) is done to a reduction of at least about 50%, preferably at least about 80%.

10 Products prepared by the process of the present invention may be vacuum brazed according to conventional techniques. These usually involve a pressure of 10^{-3} torr or less, preferably between about 10^{-4} and about 10^{-6} torr, and a temperature ranging from about 1,000°F to about 1,200°F (540-650°C), preferably from about 1060°F to about 1125°F (571°C to 607°C).

15 The following examples are offered for purposes of illustration only, and are intended neither to define nor limit the invention in any manner.

20 EXAMPLE 1

BASELINE TESTS

25 This example sets forth standards against which the product and process of the present invention may be compared. A variety of alloys, clad and unclad and of various tempers, none of which contain vanadium, were subjected to a standard corrosion test. The same test is used in the remaining examples in this specification.

For the baseline test, pieces of sheet product ranging in thickness from 0.013 inch (0.03 cm) to 0.038 inch (0.10 cm) were cut into coupons measuring 2x3 inches (5.1 x 7.6 cm). Each coupon was masked on 30 one side with electroplater's tape. The other side was intermittently exposed to an atomized corrosion solution (42 g/liter synthetic sea salt, 10 ml/liter acetic acid, balance water) in a 98% humid atmosphere for variable periods of time at a temperature of 120°F (49°C) according to ASTM Procedure No. G43. The coupons were then rinsed in cold water and cleaned in a solution of chromic and phosphoric acids (ASTM Solution No. G1) at 180°F (82°C), and baked for at least thirty minutes at 250°F (121°C) to remove 35 retained water. Each coupon was then pressurized with air at 20 psig (13.8 newtons/cm²) under water and the number of perforations which resulted was determined by counting the streams of bubbles. The number of perforations per piece was recorded as a function of the number of hours in the corrosion solution.

40 The results are shown in Table 1.1 where each entry represents a single coupon. In some cases two coupons were tested under identical conditions and the results for each are shown separated by a comma. The plus sign indicates that the actual number was above the number shown.

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TABLE 1.1
 BASELINE TEST RESULTS WITHOUT BRAZING:
 5 PERFORATIONS PER SAMPLE

	Composite			Thickness (in.)	Hours:	No. of Perforations						
	Core	Cladding	Temper			48	72	96	120	144	168	192
10	3003	-	O	0.026		0	8	12	16 ⁺			
	3003	-	H16	0.038					0		2,6	2
	3004	-	H15	0.023				0	0	6	2	
15	3004	-	H19	0.018				0	4	7	16	
	3004	-	H22	0.013		0	4,0			15 ⁺		
	3004	-	H22	0.013		9	11	16 ⁺				
20	3005	-	H25	0.018				3	6	10 ⁺	12 ⁺	
	3005	-	H25	0.018		1	10	12	15 ⁺			
	3105	-	O	0.017				0	4	20 ⁺		
25	3105	-	H15	0.017		0	0	12				
	3105	-	H18	0.0				0			6,8	
	3005	4045	H24	0.013								
	(clad side exposed)					0,1	0,0		4	2	2	
30	3003	4104	H14	0.015								
	(clad side exposed)					6	11	13	16 ⁺			
	(core side exposed)					20 ⁺	20 ⁺	20 ⁺	20 ⁺			
35	The alloys used in the tests shown in Table 1.1 had the compositions shown in Table 1.2.											

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TABLE 1.2
TEST ALLOYS

Element	Weight Percents (Balance Al)					
	3003	3004	3005	3105	4045	4104
Si	0.21	0.17	0.13	0.27	9.5	10.15
Fe	0.60	0.42	0.50	0.47	0.18	0.19
Cu	0.14	0.12	0.11	0.13	0.06	0.033
Mn	1.00	1.08	1.28	0.48	0.02	0.023
Mg	0.007	1.01	0.52	0.60	0.09	1.43
Cr	0.002	0.01	0.01	0.02	-	0.003
Zn	0.027	0.03	0.03	0.04	0.03	0.028
Ti	0.009	0.03	0.02	-	-	0.009
Bi	-	-	-	-	-	0.096

A second group of coupons, clad on one side, total thickness 0.015 in (0.038 cm) and measuring 2-3/16 x 4-3/4 inches (5.6 x 12.1 cm) was brazed while suspended vertically in a three-chamber vacuum brazing furnace at a pressure of 1×10^{-5} torr and a temperature gradually increasing to $1100^{\circ}\text{F} \pm 5$ (593°C) in twelve minutes and held at that level for two minutes. The coupons were then further cut into 2-inch (5.1-cm) squares and the nonclad side masked. The corrosion test produced the results shown in Table 1.3.

TABLE 1.3
BASELINE TEST RESULTS WITH BRAZING:
PERFORATIONS PER SAMPLE

Core	Cladding	Temper	Hours:	No. of Perforations				
				24	48	72	96	120
3003	4104	H24	12	25 ⁺	25 ⁺	25 ⁺	25 ⁺	
3003	4104	H24	0	1	13	17	25 ⁺	
		(+0.15% Cr)						
3003	4104	H14	0	0	0	1	9	
		(+0.15% Cr)						

EXAMPLE 2

50 ALUMINUM -VANADIUM ALLOY TESTS

A composite (brazing sheet) was formed from the following materials:

TABLE 2.1
 TEST COMPOSITE
Weight Percents (Balance Al)

Element	Core	Cladding
Si	0.50	12.0
Fe	0.59	0.2
Cu	0.28	0.08
Mn	1.19	0.03
Mg	0.56	0.15
Cr	0.004	-
Zn	0.026	0.02
Ti	0.002	-
V	0.26	-

The composite was hot rolled to 0.0206 inch (0.052 cm), annealed at 650°F (360°C) for 25 minutes, then cold worked to 0.0187 inch (0.047 cm, a 9.2% reduction). Pieces of the sheet were subjected to a vacuum brazing cycle as in Example 1, cut to coupons 2.5 inches (6.4 cm) square, cooled to room temperature, masked on the unclad side, and corrosion tested as in Example 1.

No leaks were detected on coupons exposed for 96 and 120 hours. Facial blisters occurred on coupons exposed for 240 hours, still without leaks.

EXAMPLE 3

ALUMINUM-VANADIUM ALLOY TESTS

This example demonstrates the effects of final cold working on corrosion susceptibility. Two composites were prepared as follows:

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TABLE 3.1
 TEST COMPOSITES

Element	Core A	Core B	<u>Cladding for both</u>
Si	0.21	0.007	12.0
Fe	0.41	0.01	0.2
Cu	0.09	0.003	0.08
Mn	1.13	0.003	0.03
Mg	0.32	0.002	0.15
Cr	0.4	-	-
Zn	0.18	-	0.02
Ti	0.08	0.01	-
V	0.247	0.247	-

For each core, both a homogenized and an as-cast ingot were prepared. All were then scalped and clad 10% on one side to form the composites.

The composites were hot rolled to 0.140 inch (0.36 cm) thickness, then cold rolled to 0.018 inch (0.046 cm). Each sheet was then cut into several portions. One portion was annealed by heating to 680°F (360°C) 5 for two hours, then cold rolled to 0.0125 inch (0.032 cm) thickness (30% reduction). Other portions were cold rolled to an intermediate thickness, annealed at 680°F for two hours, then cold rolled to 0.0125 inch such that the cold reductions after annealing approximated 20%, 15%, 10% and 5% among the various portions.

The samples were subjected to a vacuum brazing cycle as in Example 1 (the temperature this time 10 gradually rising to 1115°F (602°C) over 33 minutes), cut into coupons 2 inches (5.1 cm) square, and cooled to room temperature. Two pieces of the 5% cold reduced portions were left unbrazed.

For the corrosion test, electroplater's tape was applied to the backside of each coupon, leaving the clad size exposed. Of the unbrazed coupons, one out of each pair was taped on the core side, and the other on the clad side. The corrosion test described in Example 1 was then run. The results are listed in Tables 3.2 15 and 3.3, which include observations relating to both surface blisters and leaks.

TABLE 3.2
TEST RESULTS - COMPOSITE A

Final Cold Reduction (%)	As Cast			Homogenized		
	First Blister (hours)	Test Term (hours)	Blisters/ Leaks	First Blister (hours)	Test Term (hours)	Blisters/ Leaks
<u>Brazed:</u>						
20	120	192	>10/2			
15	144	192	>10/2			
10	144	196	1/0			
5	24	120	>10/2			
<u>Brazed:</u>						
30	72	384	6/3	144	168	6/6
20	240	312	>10/2	216	288	5/10
15	240	312	>10/2	144	216	2/3
10	264	504	6/5	192	216	1/3
5	48	192	>10/3	48	48	20/3
<u>Unbrazed:</u>						
Clad side exposed:						
5	120	168	>10/0			
Core side exposed:						
5	120	144	5/*			

* Could not be pressure tested due to roughness of surface.

TABLE 3.3
TEST RESULTS - COMPOSITE B

Final Cold Reduction (%)	As Cast			Homogenized		
	First Blister (hours)	Test Term (hours)	Blisters/ Leaks	First Blister (hours)	Test Term (hours)	Blisters/ Leaks
<u>Brazed:</u>						
20	144	196	3/5	168	196	2/0
15	168	196	1/7	144	196	7/10
10	144	196	2/4	168	196	1/0
5	144	196	1/1	168	196	6/2
<u>Brazed:</u>						
30	216	384	6/13	144	216	4/7
20	288	312	3/5	264	504	2/11
15	312	312	1/7	240	312	7/10
10	240	312	1/4	336	504	1/10
5	96	312	1/1	192	312	6/2
<u>Unbrazed:</u>						
Clad side exposed:						
5		504	0/3		504	0/0
Core side exposed:						
5		504	0/0		504	0/0

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Comparing the figures in these tables with those in Tables 1.1 and 1.3, one notices a sharp reduction in the number of leaks (perforations) despite an increase in the amount of time in the corrosion test, all due to the presence of vanadium in the core alloy. (The "Blisters/Leaks" figures represent observations taken at the end of the test term.) One also notices an increase in the number of hours before the first blister appears for samples which were given a final cold reduction with the range of approximately 10% to 20%.
45 Two unexpected improvements have thus been demonstrated.

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The foregoing description is offered primarily for illustrative purposes. It will be readily apparent to those skilled in the art that the particular materials and procedures described herein may be further varied or modified in numerous ways without departing from the spirit and scope of the invention as set forth in the
50 following claims.

Claims

55 1. An aluminium alloy,
characterised by
containing vanadium as an alloying element.

2. An aluminium alloy in accordance with claim 1, in which the vanadium comprises from 0.02% to 0.4% by weight.
3. An aluminium alloy in accordance with claim 2, in which the vanadium comprises from 0.05% to 0.3% by weight.
5. 4. An aluminium alloy in accordance with any preceding claim, further comprising at least one of silicon, magnesium and manganese.
5. An aluminium alloy in accordance with claim 4, further comprising either or both of magnesium and manganese as primary alloying elements.
6. An aluminium alloy in accordance with any preceding claim, which is an alloy of the Aluminum Associations 1XXX series.
- 10 7. An aluminium alloy in accordance with any of claims 1 to 5, which is an alloy of the Aluminum Association 3XXX and 5XXX series.
8. A brazing material comprising a core alloy and a cladding, characterised in that the core alloy comprises an aluminium-base alloy containing vanadium as an alloying element and that the cladding comprises an aluminium-base brazing alloy.
- 15 9. A brazing material in accordance with claim 8, in which the vanadium constitutes from 0.02% to 0.4% by weight of the core alloy.
10. A brazing material in accordance with claim 8 or 9, in which the core alloy is an alloy of the Aluminum Association 1XXX series.
- 20 11. A brazing material in accordance with claim 8 or 9, in which the core alloy is an alloy of the Aluminum Association 3XXX and 5XXX series.
12. A brazing material in accordance with any of claims 8 to 11, in which the brazing alloy is an alloy of the Aluminum Association 4XXX series.
- 25 13. A brazing material in accordance with any of claims 8 to 12, in which the brazing alloy contains silicon as an alloying element.
14. A brazing material in accordance with claim 13, in which the brazing alloy contains from 5% to 15% of silicon by weight.
- 30 15. An aluminium sheet product formed by rolling an aluminium-base alloy to form a sheet, annealing the sheet to a substantially strain-free state and cold working the annealed sheet, characterised in that the aluminium-base alloy contains vanadium as an alloying element and that the cold working is carried out so as to effect a reduction of the sheet product in the range from 10% to 20%.
16. A sheet product in accordance with claim 15, in which the vanadium comprises from 0.02% to 0.4% by weight of the aluminium-base alloy.
- 35 17. A brazing material formed by cladding an aluminium-base core alloy with a brazing alloy, rolling the resultant clad product to form a sheet and annealing the sheet to a substantially strain-free state, characterised in that the core alloy contains vanadium as an alloying element, that the brazing alloy is aluminium-based and that the annealed sheet product is cold worked so as to effect a reduction in the range from 10% to 20%.
- 40 18. A brazing material in accordance with claim 17, in which the vanadium comprises from 0.02% to 0.4% by weight of the core alloy.
19. A brazing material in accordance with claim 17 or 18, in which the aluminium-base brazing alloy contains from 5% to 15% by weight of silicon.
- 45 20. A method of producing an aluminium sheet product, which comprises rolling an aluminium-base alloy to form a sheet, annealing the sheet to a substantially strain-free state and cold working the annealed sheet, characterised in that the aluminium-base alloy contains vanadium as an alloying element and that the cold working is carried out so as to effect a reduction of the sheet product in the range from 10% to 20%.
- 50 21. A method in accordance with claim 20, in which the vanadium comprises from 0.02% to 0.4% by weight of the aluminium-base alloy.
22. A method in accordance with claim 21, in which the vanadium comprises from 0.05% to 0.3% by weight of the aluminium-base alloy.
- 55 23. A method in accordance with any of claims 20 to 22, in which the aluminium-base alloy further contains either or both of magnesium and manganese as primary alloying elements.
24. A method in accordance with any of claims 20 to 23, in which the aluminium-base alloy is an alloy of the Aluminum Association 3XXX series.

25. A method of producing a brazing material, which comprises cladding an aluminium-base core alloy with a brazing alloy, rolling the resultant clad product to form a sheet and annealing the sheet to a substantially strain-free state,
characterised in

5 that the core alloy contains vanadium as an alloying element and that the annealed sheet is cold worked so as to effect a reduction in the range from 10% to 20%.

26. A method in accordance with claim 25, in which the vanadium comprises from 0.02% to 0.4% by weight of the aluminium-base core alloy.

27. A method in accordance with claim 26, in which the vanadium comprises from 0.05% to 0.3% by weight of the aluminium-base core alloy.

10 28. A method in accordance with any of claims 25 to 27, in which the brazing alloy contains silicon as an alloying element.

29. A method in accordance with claim 28, in which the brazing alloy contains from 5% to 15% of silicon by weight.

15 30. A method in accordance with any of claims 25 to 29, in which the core alloy further contains either or both of magnesium and manganese as primary alloying elements.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86308368.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	<p>DE - A1 - 3 244 634 (CEGEDUR)</p> <p>* Claim *</p> <p>--</p>	1-5	C 22 C 21/00 C 22 C 21/02 B 23 K 35/04
X	<p>US - A - 3 857 165 (VERNAM)</p> <p>* Abstract; claims *</p> <p>--</p>	1-5, 8, 9, 13, 15, 16	B 23 K 35/15 C 22 F 1/04 C 22 F 1/06
X	<p>US - A - 4 284 437 (BABA)</p> <p>* Example 1; claims 1 *</p> <p>--</p>	1-5, 20, 23	C 22 F 1/06
X	<p>GB - A - 939 417 (ALUMINIUM COMPANY)</p> <p>* Example 1; claims 1, 2 *</p> <p>----</p>	1-5, 20	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 22 C 21/00 B 23 K 35/00 C 22 F 1/04
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	13-03-1987	ONDER	
CATEGORY OF CITED DOCUMENTS			
X	particularly relevant if taken alone	T : theory or principle underlying the invention	
Y	particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date	
A	technological background	D : document cited in the application	
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P	intermediate document	& : member of the same patent family, corresponding document	